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Solid-phase Oxidation of 2,4-Di-*tert*-butylphenol and 3,6-Di-*tert*-butylpyrocatechol in the Presence of Alkali and Alkaline Earth Metal Halides under Elastic Deformation*

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Abstract—Solid-phase oxidation of 2,4-di-*tert*-butylphenol to give 2,2',4,4'-*tert*-butyl-6,6'-bisphenol and of 3,6-di-*tert*-butylpyrocatechol to afford 3,6-di-*tert*-butyl-1,2-benzoquinone was performed in the presence of alkali and alkaline earth metals halides under conditions of modified extrusion. The formation of the corresponding metal 3,6-di-*tert*-butylsemiquinolates was registered by ESR method. The different behavior of chlorides, bromides, and iodides was observed and rationalized basing on the dissimilar complexing ability of halogens. The mechanism of activated oxidation was assumed.

We found formerly by an example of 2,4-di-*tert*-butylphenol (**I**) that under elastic deformations phenols could undergo solid-phase oxidation activated with inorganic salts [1]. In the system phenol **I**-NaOH-$ClCH_2CO_2H$ the composition of the products of solid-phase reaction depended on the phenol **I**: NaOH ratio. At 1:1 ratio arose 2,4-d-*tert*-butylphenoxyacetic acid (**II**), and at 4-fold excess NaOH an oxidative coupling of phenol was observed to yield 2,2',4,4'-tetra-*tert*-butyl-6,6'-bisphenol (**III**). We showed that the excessive NaOH might be replaced by NaCl, and the prevailing formation of bisphenol **III** was conserved. In the present study this effect of NaCl addition was reproduced under conditions of modified extrusion in keeping with [2]: at extrusion of an equimolar mixture phenol **I**-NaOH-$ClCH_2CO_2H$ in an excess NaCl the bisphenol **III** formed virtually quantitatively. Acid **II** in this system can be obtained only under inert atmosphere.

This result evidencing the activation of oxidative process with NaCl is worth special investigation. This observation provides a possibility to involve oxygen in solid-phase process: Low reactivity of oxygen in solid phase is well known [1].

The activating mechanism of NaCl may be of complicated character as shows the analysis of its mechanochemical behavior. The effect may combine phenomena both of physical and chemical nature: from increasing surface area and changing surface properties to creation of triboplasma. The specific feature of triboplasma is the presence of highly excited states leading to formation and separation from the lattice of charged particles and electrons [3]. NaCl in triboplasma is capable of dissociation into atoms. It is as a rule very difficult to prove this process due to spontaneous recombination into the initial NaCl. One way of revealing the process is the application of chemical traps, substances capable to form with Na or Cl atoms registered intermediates. As an example may be cited a system NaCl-Hg where the chlorine atoms arising on NaCl dissociation transform Hg into $HgCl_2$, and the free Na is dissolved in the excess Hg [4].

The above data suggest that similar processes may have some contribution into the mechanism of activated phenol oxidation.

The direct proof of the possible participation of NaCl in the activated solid-phase phenol oxidation was obtained in the study on extrusion of 3,6-di-*tert*-butylpyrocatechol (**IV**) and its orthosilicate **V** in the presence of Li, Na, K, and Mg halides. The main product of pyrocatechol reaction is 3,6-di-*tert*-butyl-

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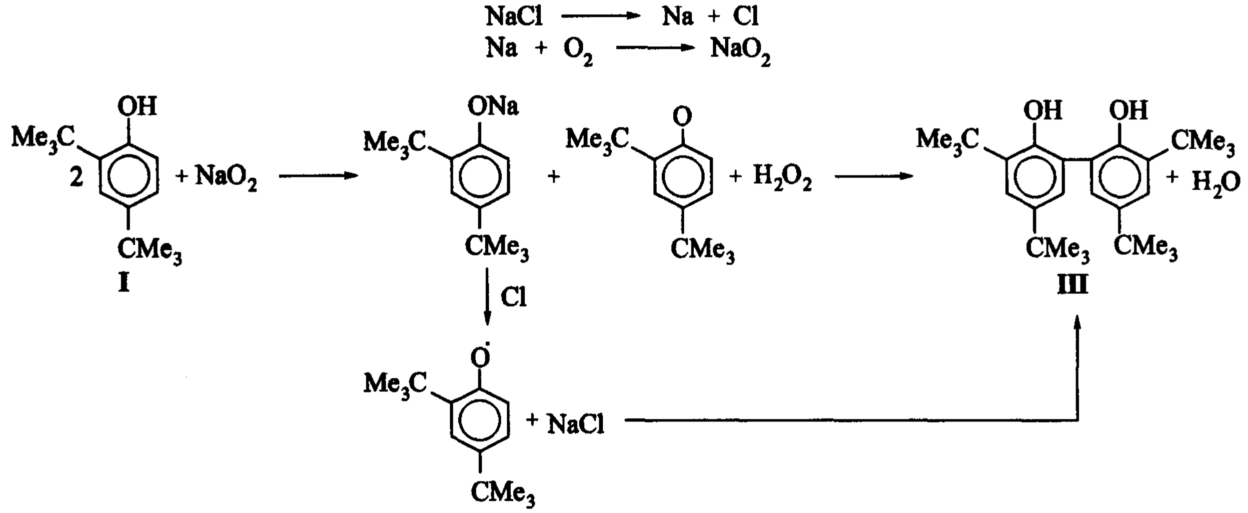
† Deceased.



1,2-benzoquinone (**VI**). However ESR study of the samples of solid-phase reaction mixtures of pyrocatechol with metal chlorides revealed signals in the form of single lines. On extraction with THF the signals transform into ESR spectra corresponding to metal 3,6-di-*tert*-butylsemiquinolates (**VII**). In all cases a triplet is observed due to coupling with two equivalent protons of the ring (a_H 3.3 Oe); with Li and Na each component of the triplet is split into quartet due to interaction with magnetic nuclei of cations (*J* 3/2, Fig. 1). In the system orthosilicate **V**–NaCl after extrusion were registered paramagnetic species. The spectrum of the species corresponded to the adduct of ester **V** with chlorine atom described previously in [5]: alternating-broadened quintet due to interaction of the lone electron with four protons of the pyrocatechol ligands (a_H 2.2 Oe, Fig. 2).

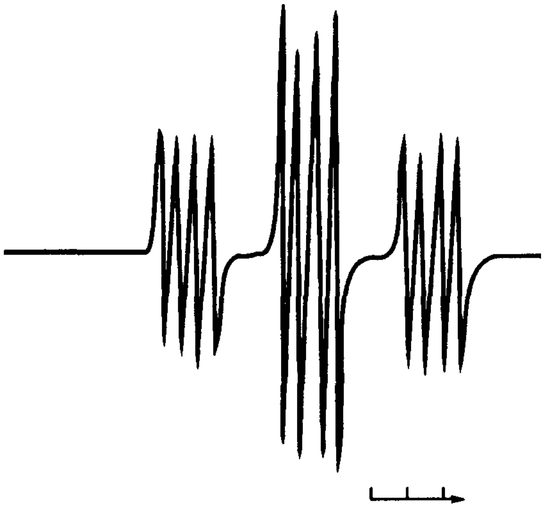


Fig. 1. ESR spectrum of sodium 3,6-di-*tert*-butyl-*ortho*-benzosemiquinolate obtained at extrusion of 3,6-di-*tert*-butylpyrocatechol in NaCl environment. THF, *T* 300 ¤.

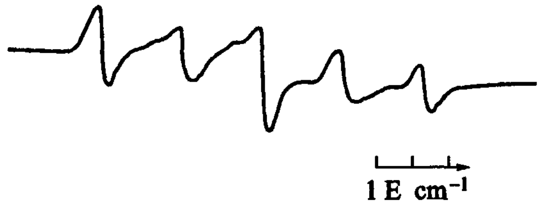
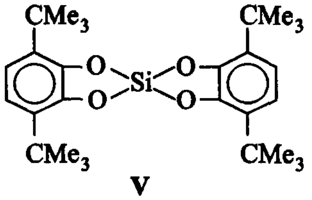
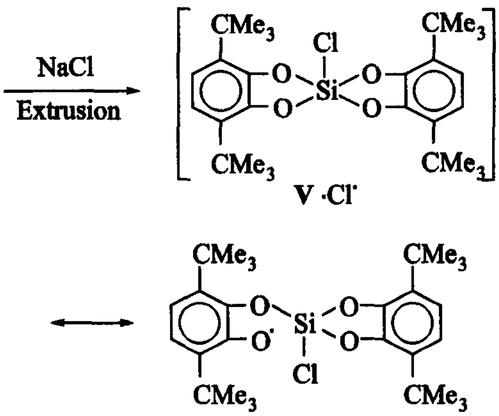


Fig. 2. ESR spectrum of the radical formed at extrusion of orthosilicate of 3,6-di-*tert*-butylpyrocatechol in NaCl environment.

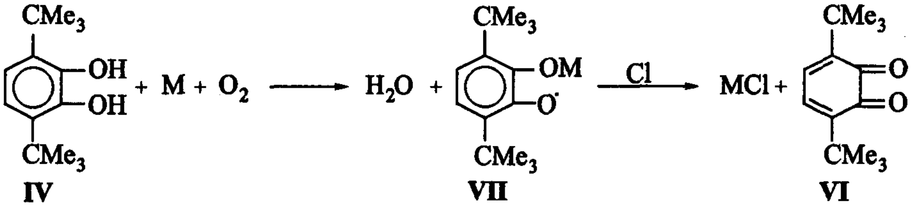


V



These observations provide a possibility to suggest the oxidation mechanism of pyrocatechol **IV** including the participation of MCl in the catalytic

$$MCl \longrightarrow M + Cl$$



cycle with the intermediate semiquinolate (**VII**) formation.

An alternative exchange mechanism including replacement of HCl and its elimination from the reaction site and from further participation in the catalytic cycle (ArOH+NaCl→ArONa + HCl↑ etc.) seems a lot less probable, since in this case should accumulate alkali that is not observed experimentally. Another objection against the exchange mechanism lies in the data of [6] where has been demonstrated that quinone **VI** treated with HCl is reduced to pyrocatechol **IV**.

The appearance of spectrum from semiquinolate **VII** depends on the halide in the metal halide. The ESR spectra were observed only with chlorides. Presumably with bromides and iodides operates cryptoradical mechanism where semiquinolate does not appear as a kinetically independent species.

$$\mathbf{IV} + MX + O_2 \rightarrow H_2O + [\mathbf{VII} + X] \rightarrow \mathbf{VI} + MX$$

It is interesting to note that in reactions with iodides the reaction mixtures have intense blue color. In the absence of colored paramagnetic compounds it can be understood as formation of solid-phase charge-transfer complexes between quinone **VI** and iodide-ion. On treating with the organic solvent the complexes are decomposed, and the solutions turn brown-green as characteristic of quinone. Apparently in the systems under study complex formation is very important, and the observed dissimilar behavior of halides may be due to unlike capability of halogens to complexing; the latter determines the stability of the reaction cage [**VII**+ X].

EXPERIMENTAL

ESR spectra of solid samples or of solutions in THF or toluene freed from oxygen were registered on spectrometer Varian E-12A. The concentration of paramagnetic species estimated by comparison with reference 4-hydroxy-2,2'6,6'-tetramethylpiperidin-1-oxyl amounted to ~10^{17} spin/g (~0.1%). TLC analysis of the reaction mixtures was carried out in the system hexane–ethyl ether, 4:1, on Silufol UV-254 plates.

The solid compositions were prepared by mixing reagents ($5\text{-}10^{-3}$ mol) with excess (~20 g) of metal halide of chemically pure grade (LiCl, NaCl, KCl, $MgCl_2$, NaBr, KBr, NaI, KI), and the mixture was subjected to modified extrusion procedure in a worm device described in [2], or to grinding in an agate mortar in air on in a chamber filled with argon. The deformation stability of the initial phenol **I**, pyrocatechol **IV**, and ester **V** was estimated by extrusion or grinding in a mortar with subsequent analysis by TLC. No products of oxidation, isomerization, or dealkylation were observed in any case.

A mixture of equimolar quantities of phenol **I**, $ClCH_2CO_2H$, NaOH (per $5\text{-}10^{-3}$ mol each) in 20 g of NaCl was subjected to extrusion for 30 min. The sample was treated with water acidified with HCl, extracted with chloroform, and dried with anhydrous $MgSO_4$. On removing the solvent and crystallization we obtained 0.9 g (90%) of bisphenol **III**, mp 208–209°C (from methanol); the melting point corresponded to that in [1]. Two samples of the reaction mixture prepared as above, 0.5 g each, were ground in an agate mortar for 15 min : the first sample in air, the second one under argon. The samples were analyzed by TLC. In the first sample alongside the initial phenol was detected bisphenol **III**, in the second sample formed acid **II**. Reference sample of acid **II** was prepared as in [1], mp 178–179°C (from hexane–chloroform).

A mixture of pyrocatechol IV ($5\text{-}10^{-3}$ mol) with 20 g of metal halide was subjected to extrusion for 30 min. From 2 g of the reaction mixture was isolated 0.03-0.04 g (50–35%) of quinone **VI**, mp 199-200°C (from hexane) in agreement with [7].

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